

Dimethylglyoxime based ion-imprinted polymer for the determination of Ni(II) ions from aqueous samples

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Abstract

A Ni(II)-dimethylglyoxime ion-imprinted polymer {Ni(II)-DMG IIP} was synthesised by the bulk polymerisation method. The morphology of the Ni(II)-DMG IIP and non-imprinted polymer were observed by scanning electron microscopy and the chemical structures were evaluated by infrared spectroscopy. Selectivity of the Ni(II)-DMG IIP was studied by analysing, using an inductively coupled plasma-optical emission spectrometer, for Ni(II) ions that were spiked with varying concentrations of Co(II), Cu(II), Zn(II), Pd(II), Fe(II), Ca(II), Mg(II), Na(I) and K(I) in aqueous samples. The studies revealed Ni(II) recoveries ranging from 93 to 100% in aqueous solutions with minimal interference from competing ions. Enrichment factors ranged from 2 to 18 with a binding capacity of $120 \mu\text{g}\cdot\text{g}^{-1}$. Co(II) was the only ion found to slightly interfere with the determination of Ni(II). Selectivity studies confirmed that the Ni(II)-DMG IIP had very good selectivity, characterised by %RSD of less than 5%. The limits of detection and quantification were $3\times 10^{-4} \mu\text{g}\cdot\text{mL}^{-1}$ and $9\times 10^{-4} \mu\text{g}\cdot\text{mL}^{-1}$, respectively. The accuracy of the method was validated by analysing a custom solution of certified reference material (SEP-3) and the concentration of Ni(II) obtained was in close agreement with the certified one. The Ni(II)-DMG IIP was successfully employed to trap Ni(II) ions from a matrix of sea, river and sewage water. It is believed that the Ni(II)-DMG IIP has potential to be used as sorbent material for pre-concentration of Ni(II) ions from aqueous solutions by solid-phase extraction.

Keywords: nickel, polymer, dimethylglyoxime, interference

Introduction

Heavy metals are stable and cannot be degraded or destroyed easily (Zheng et al., 2007; Prechthai et al., 2008; Yao et al., 2009). They therefore tend to accumulate in the environment, from where they eventually get into the human food chain. The human body needs some of these metals at trace levels but further accumulation in the body results in various health effects (Singh et al., 2010; Wang et al., 2005; Khan et al., 2008). It is therefore important to determine their levels in the environment. This is especially important for water, where heavy metal contamination is prevalent (Momodu and Anyakora, 2010; Mansour and Sidky, 2002; Rico et al., 1989; Miller et al., 2004; Dhakate and Singh, 2008). However, the determination of heavy metals in water samples is rather challenging as they occur at low concentration levels in complex matrices (Ubalua et al., 2007; Hlavay et al., 2004; Namiešnik, 2002; Winkler et al., 1991; Dheri et al., 2007). Hence, there is the need to remove the matrices or develop pre-concentration strategies that can enhance selectivity prior to their determination in water samples (Tan and Huang, 2009; Li and Zhou, 2006).

Various pre-concentration techniques, such as normal digestion (Balcerzak, 2002; Rechcigl and Payne, 1989), microwave digestion (Rechcigl and Payne, 1989; Sarin et al., 2004), slurry techniques (Lima et al., 2000), chemical precipitation (Massoumi and Hedrick, 1969), electro-deposition (Ruotolo and Gubulin, 2002), cementation (Chang et al., 2007),

ultra-filtration (Hong et al., 1998), ion exchange (Shao et al., 1991), activated carbon adsorption (Wilson et al., 2006), liquid-liquid extraction (Sarma and Reddy, 2002) and solid-phase extraction (SPE) (Hennion, 1999), have been used to abstract trace metals from matrices. These methods have the limitation of poor selectivity as one sorbent normally picks up several metal ions at once (Pourreza et al., 2010). SPE can be combined with ion-imprinted polymers (IIPs) in order to improve selectivity of ions (analytes) of interest from environmental samples (Ramakrishnan and Rao, 2006; Otero et al., 2009; Romani et al., 2009a; Romani et al., 2009b; Zhu et al., 2009; Krishna et al., 2004).

Ion-imprinted polymers (IIPs) are highly selective cross-linked polymeric materials, synthesised by complexing a template (metal ion) and a functional monomer in the presence of a crosslinker (Nishide et al., 1976). The reaction proceeds via a free radical initiator in an appropriate solvent normally referred to as a porogen. Removal of the template creates cavities that are complementary in size and charge to the metal of interest. The memory is a result of the effect of the size and charge of the metal ion that was present in the cavity during polymerisation. Hence the cavities have a high recognition/selectivity for the metal ion only. The functional mechanism is similar to that of antibodies or enzymes. However, IIPs have advantages over antibodies in that they are cheap and can be used in or with a variety of solvents at high temperature, pressure and pH, which antibodies or enzymes would not tolerate.

Due to their high selectivity, IIPs have been used as sorbents in SPE (Rao et al., 2004). Such sorbents have an advantage over conventional SPE sorbents in that they can be used in a variety of solvents at high temperature and pressure, and over a wide pH range, without compromising on their efficiencies. IIP-SPE combines the advantages of SPE, such as low cost, speed, simplicity and flexibility, with the high selectivity of

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IIPs (Wilson et al., 2006). Of all the methods used in preparing IIPs, the trapping method is the most commonly used (Romani et al., 2008; Praveen et al., 2005; Metilda et al., 2007; James et al., 2009; Daniel et al., 2003; Romani et al., 2009a; Romani et al., 2009b; Uguzdogan et al., 2010; Saraji and Yousefi, 2009). This is because other methods require the use of a complexing ligand having vinyl groups (Ersoz et al., 2004; Li et al., 2005; Su et al., 2007; Jiang et al., 2006; Chen et al., 2009), which are scarce.

Nickel is one of the most widely imprinted ions. It is imprinted by different methods of polymerisation. Most nickel ion-imprinting studies have been carried out using the trapping method (Romani et al., 2008; Praveen et al., 2005; Daniel et al., 2003; Romani et al., 2009a, Romani et al., 2009b; Jiang et al., 2006; Singh and Mishra, 2010), with different chelating agents such as hydroxyquinoline (Otero et al., 2009; Romani et al., 2009a; Zhu et al., 2009; Romani et al., 2008) or modified hydroxyquinoline (Romani et al., 2009) and its derivatives (mainly 5,7-dichloroquinoline) (Praveen et al., 2005), and dithizone (Saraji and Yousefi, 2009). Other methods, such as surface imprinting and chemical immobilisation, have also been employed (Su et al., 2007; Jiang et al., 2006; Chen et al., 2009; Vijaya et al., 2008). However, dimethylglyoxime (DMG) has rarely been used as a ligand in these ion-imprinting polymerisation reactions. DMG has been used for the determination of nickel using colourimetric and gravimetric techniques (Gazda et al., 2004; Ali et al., 1999; Willard, 1943; Qureshi et al., 2008; Korolczuk, 2000, Van Den Berg and Nimmo, 1987). Daniel et al., 2003, designed a Pd(II)-DMG IIP for the selective uptake of palladium ions from dilute aqueous solutions. The total time needed to prepare the polymer was more than 2 days. Therefore, new methods are needed to reduce this period of time if DMG-based ion-imprinted polymers are to be successfully used as SPE sorbents for the determination of Ni(II).

In this paper, we report the synthesis of a DMG-based Ni(II) ion-imprinted polymer {Ni(II)-DMG IIP} that can be used to selectively trap Ni(II) ions in aqueous solutions in the presence of competing cations. To the best of our knowledge, no Ni(II) ion imprinting work has been reported using DMG as the trapped ligand.

Experimental

Chemicals and reagents

Analytical grade sodium hydroxide pellets, hydrochloric acid/potassium chloride buffer solution, disodium hydrogen phosphate buffer solution, acetic acid (glacial), sodium acetate buffer solution, 4-vinylpyridine, 2,2'-azobisisobutyronitrile (AIBN), 2-methoxy ethanol, styrene, nickel(II) sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), divinyl benzene (DVB), dimethylglyoxime (DMG), trace metal grade nitric acid, hydrochloric acid and stock solutions of Ni(II), Cu(II), and Co(II) were obtained from Sigma Aldrich (Steinheim, Germany). Pd(II) was obtained from BDH laboratories Chemical Division (London, UK). Standard solutions of Ca(II), Fe(II), Mg(II), Zn(II), Na(I), and K(I) were freshly prepared from their nitrate salts also obtained from Sigma Aldrich. Filter paper was acquired from Whatman (Maidstone, UK). An A10 milli-Q system from Millipore RiOs (Bedford, USA) was used to generate ultrapure water. A custom solution of certified reference material (CRM), SEP-3 was obtained from Inorganic Ventures (Christiansburg, USA).

Instrumentation

Scanning electron microscopy (SEM) images were acquired by a TS5136ML Digital Vega Microscope from Tescan (Brno, Czech Republic). FTIR ($400\text{--}4\,000\text{ cm}^{-1}$) spectra were recorded on a PerkinElmer Spectrum 100 spectrometer (Massachusetts, USA) equipped with a universal ATR sampling accessory. Concentrations of metals were determined using an iCAP 6000 series inductively coupled plasma-optical emission spectrometer (ICP-OES) from Thermo Electron Corporation (Cheshire, United Kingdom). The solution pH was measured using the Jenway 3510 pH meter (Essex, UK).

Preparation of the Ni(II)-DMG IIP

Ni(II)-DMG IIP was prepared by mixing $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (0.263 g), 4-VP (0.23 ml) and DMG (0.465 g) in 2-methoxy ethanol (10.0 ml) with stirring for 10 min, to form a ternary complex. Subsequently, DVB (1.78 ml), styrene (1.15 ml) and AIBN (50.0 mg) were added. The mixture was cooled to 0°C and purged with nitrogen gas for 10 min. Polymerisation was carried out by heating in an oil bath at 70°C for 3 h. The red-coloured Ni(II)-DMG IIP was then homogenised using a pestle and mortar to obtain a fine powder. The powder was sieved through a $45\ \mu\text{m}$ mesh before it was subsequently washed 3 times with 50% HCl and then 3 times with ultrapure water. The leached Ni(II)-DMG IIP was then dried at 55°C for 12 h. The NIP was prepared by the same procedure except that $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was omitted.

Sample collection and preparation

Sea, river, untreated sewage and treated sewage water samples were collected in polyethylene containers by a grab sampling method. 100.0 ml portions of water samples doused with 2.0 ml conc. HNO_3 and 5.0 ml conc. HCl were digested by heating on a hot plate at 90°C until the volume was reduced to 20.0 ml. The solution was then filtered through Whatman No. 1 filter paper, after allowing it to cool, and diluted to 100.0 ml with ultrapure water prior to ICP-OES analysis (Method 3005A, 1992).

Optimisation of pH

The concentration of hydrogen ions is very important in IIPs because, as mentioned earlier, the selectivity of IIPs is based on size and charge. Therefore, high concentrations of the hydrogen ions interfere with the rebinding of the metal ion (Kempe and Kempe, 2010) to the cavity, as the hydrogen ions also bind with the cavity, and a low concentration of hydrogen ions means there are a lot of hydroxides, which usually form precipitates with metals even under slightly acidic conditions (Athikomrattanakul et al., 2009). Hence it is very important to optimise pH in order to have maximum rebinding of metal ions on the cavity. A set of 3 replicates of 30.0 ml portions of $10\ \mu\text{g}\cdot\text{mL}^{-1}$ Ni(II) solutions were prepared and their pH adjusted from 1.0 to 12.0. From pH 1 to 3, the hydrochloric acid/potassium chloride buffer was used, for pH 4 to 6, sodium acetate buffer was used, and for pH 7 to 12, the disodium hydrogen phosphate buffer was used. Then 40.0 mg of Ni(II)-DMG IIP was added into each solution and stirred for 5 min.

Optimisation of mass

Sorbents or imprinted polymers have loading capacities (Genhua et al., 2010) – the concentration of metal ions per

mass of sorbent. Therefore, it is important to know the mass of sorbent needed per volume of sample, in order to avoid using too much of sorbent or wasting sorbent when a low mass can be used. However, adding a low mass of sorbent will compromise the results obtained. For mass optimisation, 10.0 to 100.0 mg of leached Ni(II)-DMG IIP were weighed into each solution and stirred for 30 min.

Optimisation of time

Time is important in rebinding studies as sufficient time should be allowed for the metal ion to rebind to the sites. This is mainly because the binding sites are sometimes not on the surface; hence time is required for metal ions to move towards binding sites (Piletsky et al., 2010). To optimise for time needed for Ni(II) rebinding, equal volumes of Ni solutions (30.0 mL) were used and adjusted to pH 8.0. Times for rebinding of Ni(II), ranging from 15 s to 1 800 s, were evaluated.

Recyclability

To test for reusability of the IIP, 3 replicates of 30.0 mL portions containing $10 \mu\text{g}\cdot\text{mL}^{-1}$ Ni(II) were taken, buffered with disodium hydrogen phosphate and their pH adjusted to 8.0. Then 50.0 mg of a leached Ni(II)-DMG IIP was weighed into each solution and stirred for 5 min. The Ni(II)-DMG IIP was evaluated for reuse 6 times.

In all of the experiments, the amount of Ni(II) absorbed by Ni(II)-DMG IIP was desorbed with 50% HCl and the concentration of Ni(II) quantified by ICP-OES. This value was in all cases not significantly different from the one obtained by taking the reduction in concentration of the Ni(II) solution as the amount trapped by the Ni(II)-DMG IIP. The percentage extraction efficiency was then calculated as shown in Eq. (1):

$$\%EE = \left(\frac{C_i - C_s}{C_i} \right) \times 100 \quad (1)$$

where:

C_i is the initial solution concentration ($\mu\text{g}\cdot\text{mL}^{-1}$) and
 C_s is the solution concentration after adsorption.

Selectivity and interference studies

For selectivity, 50.0 mg of leached Ni(II)-DMG IIP or NIP material was placed into 30.0 mL portions of $10 \mu\text{g}\cdot\text{mL}^{-1}$ solutions of Ni(II), Mg(II), Ca(II), Na(I), K(I), Co(II), Cu(II), Zn(II), Fe(II) and Pd(II), which were then stirred for 5 min. The Ni(II)-DMG IIP was filtered off and the change in metal concentration was taken as the amount trapped by the Ni(II)-DMG IIP or NIP. The recoveries of each metal were calculated after quantification with ICP-OES. For interference, 50.0 mg Ni(II)-DMG IIP was placed into 30.0 mL aliquots of each of $10 \mu\text{g}\cdot\text{mL}^{-1}$ Ni(II), Mg(II), Ca(II), Na(I), K(I), Co(II), Pd(II), Cu(II), Zn(II) and Fe(II), which were then stirred for 5 min. The concentration of Ni(II) was kept at $10 \mu\text{g}\cdot\text{mL}^{-1}$, while the concentrations of Mg(II), Ca(II), Na(I), K(I), Co(II), Pd(II), Cu(II), Zn(II) and Fe(II) were varied from 10 to $20 \mu\text{g}\cdot\text{mL}^{-1}$ in successive experiments. A mixture containing $10 \mu\text{g}\cdot\text{mL}^{-1}$ of Mg(II), Ca(II), Na(I) and K(I) was also prepared and the interference on Ni(II) recovery at $10 \mu\text{g}\cdot\text{mL}^{-1}$ and $20 \mu\text{g}\cdot\text{mL}^{-1}$ of these metal ions was evaluated. Lastly, a solution containing all of the above elements was prepared at $10 \mu\text{g}\cdot\text{mL}^{-1}$ and at $20 \mu\text{g}\cdot\text{mL}^{-1}$ and

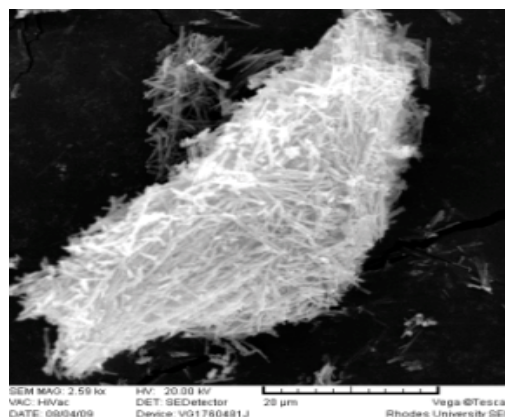


Figure 1
SEM image of a Ni(II)-dimethylglyoxime complex

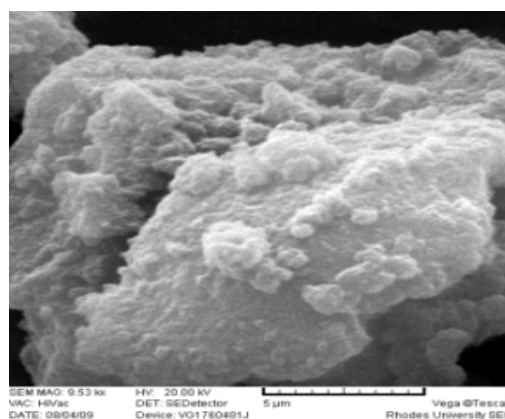


Figure 2
SEM image of an imprinted polymer

the interference of the elements in this solution with recovery of Ni(II) was tested at these levels. The effect of Co(II) and Cu(II) on the recovery of Ni(II) and the interaction between the two were evaluated using the scheme outlined by Montgomery et al. (2005).

Results and discussion

Characterisation of the morphology of the polymers

Figure 1 shows the SEM images of the Ni(II)-dimethylglyoxime complex, Fig. 2 is Ni(II)-DMG IIP, Fig. 3 is NIP and Fig. 4 is leached DMG IIP. The morphology of the Ni(II)-DMG complex was fibrous while that of Ni(II)-DMG IIP had more agglomerates; the NIP was spongier and the leached Ni(II)-DMG IIP had a more porous morphology. Literature has shown that IIPs prepared by bulk polymerisation are large-sized swollen irregular agglomerates, whereas the NIP consists of agglomerates and also spherical monodisperse particles, whilst the leached IIP is expected to have some cracks and pores on the surface (Romani et al., 2008; Romani et al., 2009a; Uguzdogan et al., 2010; Vijaya et al., 2008; Tokalioglu et al., 2009; Arani et al., 2008; Esen et al., 2009; Daniel et al., 2005). In this case, the spongier morphology of the NIP shows that it is 'relaxed' and has the ability to absorb Ni(II) ions and become 'stiff' like Ni(II)-DMG IIP. The morphology of the Ni(II)-DMG complex is expected to show needle-like structures

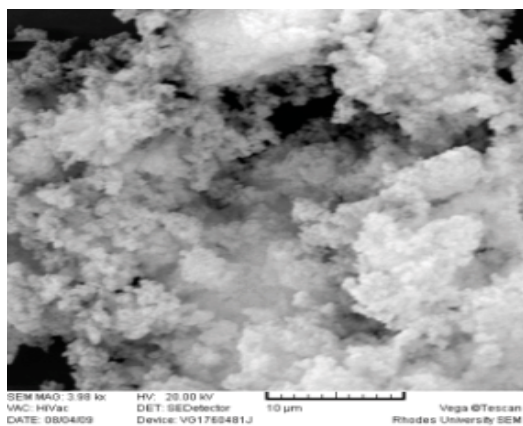


Figure 3
SEM image of a non-imprinted polymer

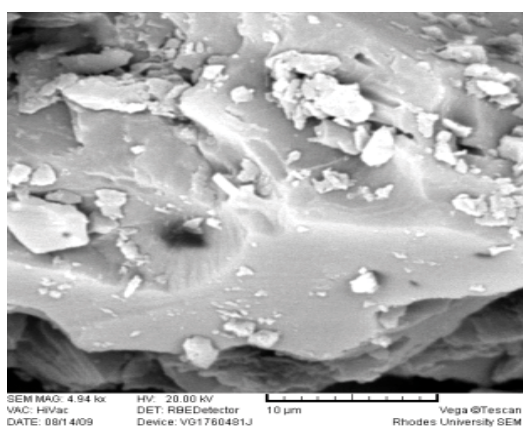


Figure 4
SEM image of a leached imprinted polymer

with a diameter of about 200 nm and a length of up to several micrometers (Ni et al., 2006; Kordatos et al., 2009), which is what was observed.

IR studies

The IR spectrum of Ni(II)-DMG IIP in Fig. 5C indicates that Ni(II) is bound through the nitrogen atoms due to the change in (C=N) from around 1 636 cm⁻¹ and 1 638 cm⁻¹, respectively, in the free DMG (as shown in Fig. 5A) and NIP (as shown in Fig. 5B) to 1 628 cm⁻¹ in the Ni(II)-DMG IIP (as shown in Fig. 5C). The IR spectrum of the Ni(II)-DMG IIP (as shown in Fig. 5C) also shows the presence of an OH deformation band at 1 737 cm⁻¹, indicating the formation of a hydrogen bridge (Burger et al., 1965; Cardoso et al., 2009; Nyquist et al., 2001; Panja et al., 1991). This hydrogen bridge confirms the formation of the red square planar Ni(II)-DMG IIP complex and is absent in the DMG and in the NIP (as shown in Figs. 5A and 5B).

Optimisation of pH

At pH 0 to 4.0 the recoveries ranged from 13 to 24%; good recoveries (72-89%) were recorded in the pH range of 6.0 to 10.0, and beyond pH 10.0 the recovery dropped (Fig. 6). The pH range determined for optimal rebinding of Ni(II) is in

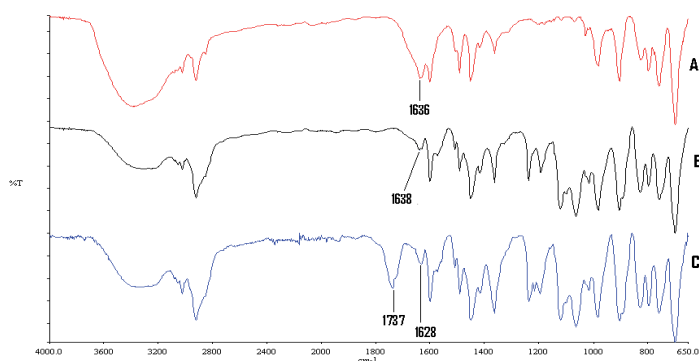


Figure 5
IR spectra of DMG (A), DMG-NIP (B) and Ni(II)-DMG-IIP (C)

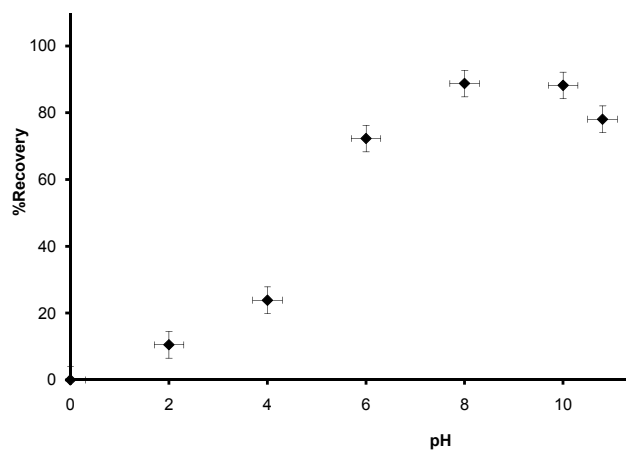


Figure 6
Effect of pH on recovery of Ni(II)

agreement with that reported in literature (Otero et al. 2009; Romani et al., 2009^a; Romani et al., 2008; Romani et al., 2009b; Praveen et al., 2005; Uguzdogan et al., 2010; Saraji and Yousefi, 2009; Ersoz et al., 2004; Chen et al., 2009; Gazda et al., 2004; Panja et al., 1991). Ni(II) is better adsorbed by DMG at higher pH values. This is because it is the conjugate base of DMG which complexes the metal ions. At lower pH values, DMG is protonated and cannot bind effectively with metals. Its binding capacity is enhanced when it is deprotonated at higher pH values.

Optimisation of mass

50.0 mg of leached ion-imprinted polymer was found to be the optimal mass of the Ni(II)-DMG IIP needed to achieve the maximum recovery of 98% (as shown in Fig. 7), and therefore 50.0 mg was used in this study, making up a polymer-to-solution ratio of 5:3. The Ni(II)-DMG IIP performed exceptionally well, compared to some other IIPs, as it used lower quantities of polymer per volume of sample (Romani et al., 2008; Romani et al., 2009a; Ersoz et al., 2004; Singh and Mishra, 2010), taking into consideration the higher concentrations of samples that were used in this study. The concentration ($\mu\text{g}\cdot\text{mL}^{-1}$) of a metal ion bound to the IIP, referred to as binding capacity, Q , is calculated as shown in Eq. (2):

$$Q = \frac{V(C_i - C_s)}{W} \quad (2)$$

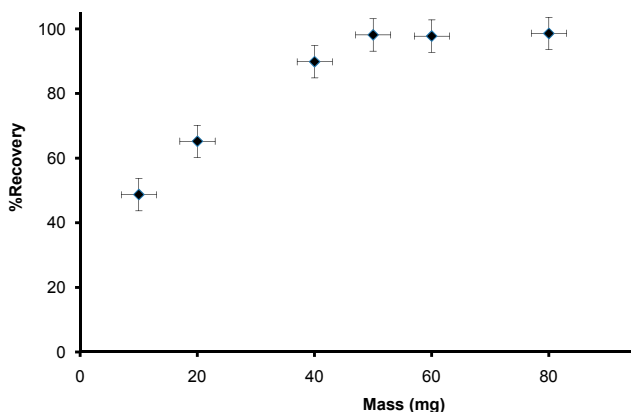


Figure 7

Effect of mass on recovery of Ni(II) for Ni(II)-DMG-IIP

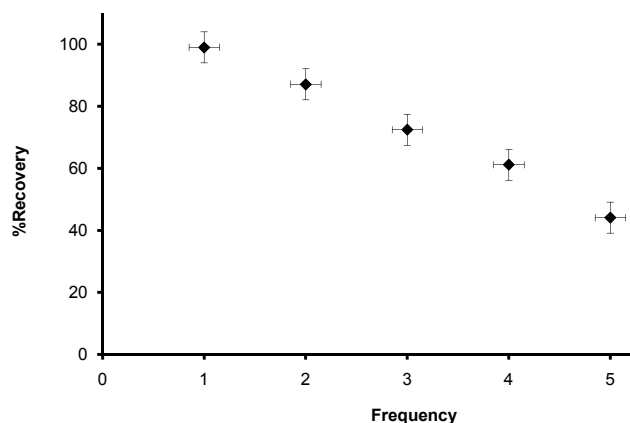


Figure 8

Effect of repeated use on recovery of Ni(II)

where:

V is the volume of the solution (mL)

C_i is the initial solution concentration ($\mu\text{g}\cdot\text{mL}^{-1}$)

C_f is the solution concentration after adsorption

W is the mass(g) of the polymer used for extraction.

The exact value for the Ni(II)-DMG IIP was found to be $120 \mu\text{g}\cdot\text{g}^{-1}$.

Reusability and kinetics of the ion-imprinted polymer

Although some IIPs have been reported to be reusable (Otero et al., 2009; Romani et al., 2009a; Rao et al., 2004; Daniel et al., 2003), the percentage recovery of Ni(II)-DMG IIP dropped from 98% to 44% upon the sixth usage (as shown in Fig. 8). This is, however, not a major limitation as the solid-phase extraction sorbents, which are the ultimate goal of synthesising this IIP, are used only once. A maximum of 1 min was the time needed to rebind all the nickel ions onto imprinted sites of the Ni(II)-DMG IIP. Considering the time taken by other polymers, i.e. 2 min (Otero et al., 2009), 5 min (Praveen et al., 2005; Jiang et al., 2006) and 20 min (Uguzdogan et al., 2010), this Ni(II)-DMG IIP showed good kinetics of rebinding.

Selectivity and interference studies

The recovery of Ni(II) was much higher than that of Co(II), Cu(II), Zn(II), Pd(II), Ca(II), Mg(II), Na(I) and K(I), demonstrating that the cavities in the Ni(II)-DMG IIP had higher affinity for Ni(II), as shown in Table 1. The %EE was calculated using Eq. (1). Despite the fact that Fe(II), Co(II) and Cu(II) (Zen and Lee, 1993; Ershova and Ivanov, 2000; De Sousa and Korn, 2001) are known to interfere with the complexation of nickel with DMG, these metals did not show any interference with the extraction efficiency of Ni(II) when the Ni(II)-DMG IIP was used. Although DMG is selective for both Pd(II) and Ni(II), it seems that in this case Ni(II)-specific cavities were created. This was evidenced by the lower extraction efficiencies recorded for Co(II), Cu(II), Zn(II) and Pd(II), which have about the same size and charge as Ni(II). Fe(II) had a reasonably high recovery but did not interfere with the determination of Ni(II).

The selectivity of the Ni(II)-DMG IIP for Ni(II) in this study was much better than that previously reported for some polymers (Romani et al., 2009a; Praveen et al., 2005; Romani et al., 2009b). Zn(II), Pd(II), Fe(II), Ca(II), Mg(II), Na(I) and K(I) in the water samples did not interfere with the binding of Ni(II) on the IIP, as shown in Table 2. To compute the main

Table 1
The % extraction efficiency (%EE) of Ni(II) IIPs obtained from other sources compared to Ni(II)-DMG-IIP (*denotes an IIP was for palladium and is only shown here because DMG was used as a trapped ligand; the values in brackets are for non-imprinted polymers).

IIP	% EEs									
	Ni(II)	Fe(II)	Co(II)	Pd(II)	Cu(II)	Zn(II)	Ca(II)	Mg(II)	Na(I)	K(I)
This work (n=3)	98 (66)	100 (100)	62 (37)	26 (22)	37 (42)	37 (37)	38 (59)	47 (62)	64 (62)	37 (52)
Ni(II)-Hydroxyquinoline (Otero et al., 2009)	99 (1)	82 (84)	-	-	93 (39)	90 (37)	-	-	-	-
Ni(II)-Hydroxyquinoline (Romani et al., 2009a)	99 (10)	-	-	-	99 (23)	99 (19)	-	-	-	-
Pd(II)-Dimethyl glyoxime (Daniel et al., 2003)*	2 (2)	-	-	99 (48)	2 (2)	1 (1)	-	-	-	-
Ni(II)-Bifunctionalised 5-vinyl-HQ (Romani et al., 2009b)	99 (73)	84.8 (85)	63 (60)	-	75 (76)	71 (74)	-	-	-	-
Ni(II)-Dithizone (Saraji and Yousefi, 2009)	93 (37)	-	14 (8)	-	62 (68)	-	-	-	-	-

Element(s) added	Concentrations of elements added ($\mu\text{g}\cdot\text{mL}^{-1}$)	Concentration of Ni(II) ($\mu\text{g}\cdot\text{mL}^{-1}$)	% Recovery
Na(I)	10, 20	10	96, 98
K(I)	10, 20	10	98, 99
Ca(II)	10, 20	10	91, 93
Mg(II)	10, 20	10	91, 93
Ca(II), Mg(II), Na(I) and K(I)	10, 20	10	98, 94
Co(II)	10, 20	10	93, 81
Pd(II)	10, 20	10	90, 89
Cu(II)	10, 20	10	92, 87
Zn(II)	10, 20	10	93, 89
Fe(II)	10, 20	10	94, 91
All above	10,20	10	83, 74
Co(II); Cu(II)	10, 10	10	91
Co(II); Cu(II)	10, 20	10	92
Co(II); Cu(II)	20, 10	10	89
Co(II); Cu(II)	20, 20	10	87

effect of Cu(II) on Ni(II) for the 2 factorial design experiments, the average response in all runs with Cu(II) at the high setting was computed and the average response of all runs with Cu(II) at the low setting were subtracted (Montgomery, 2005). The same procedure was followed to evaluate for the main effect of Co(II). Cu(II) and Co(II) interfered with the rebinding of Ni(II); the results of interaction studies performed with these ions are shown in Table 2 (the last 4 entrants). Co(II) interfered slightly with the determination of Ni(II) and the interference of Cu(II) on Ni(II) was low. According to Montgomery (2005), for an effect to be taken as significant, it has to be greater than 5 – the effect of Co(II) on Ni(II) was less than 5 (at -3.5). Most Ni(II) ion imprinting work does not have these data, which can help to evaluate the effect of Co(II) on rebinding of Ni(II), as the 2 ions compete severely (Griffing et al., 1947; Yang and Black, 1994; Kumbasar and Sahin, 2008).

Limit of detection and limit of quantification.

The evaluated limit of detection (LOD) and limit of quantification (LOQ) were rather low, 3×10^{-4} and $9 \times 10^{-4} \mu\text{g}\cdot\text{mL}^{-1}$, respectively,

IIP	LOD ($\mu\text{g}\cdot\text{mL}^{-1}$)	LOQ ($\mu\text{g}\cdot\text{mL}^{-1}$)
This work (n=3)	3.00×10^{-4}	9.00×10^{-4}
Ni(II)-Hydroxyquinoline (Otero et al., 2009)	3.30×10^{-4}	1.10×10^{-3}
Ni(II)-Hydroxyquinoline (Romani et al., 2009a)	1.40×10^{-4}	4.70×10^{-4}
Ni(II)-Hydroxyquinoline (Romani et al., 2008)	5.00×10^{-5}	
Ni(II)-Bifunctionalised 5-vinyl-HQ (Romani et al., 2009b)	2.60×10^{-4}	8.70×10^{-4}
Ni(II)-Dithizone (Saraji and Yousefi, 2009)	1.60×10^{-3}	-
Ni(II)-Amino-functionalised silica gel (Jiang et al., 2006)	1.60×10^{-4}	-
Ni(II)-Methacryloyl histidine-dihydrate (Ersoz et al., 2004)	3.00×10^{-4}	-

and very low compared to some previously reported values, as shown in Table 3. Those with both lower LOD and LOQ than the Ni(II)-DMG IIP had lower selectivity for Ni(II) or higher interference from closely-related ions or high %RSD values (Romani et al., 2009a; Praveen et al., 2005; Romani et al., 2009b).

Analysis of CRM

The developed method was validated by analysing a custom solution of CRM of water (SEP-3), as shown in Tables 4 and 5. The results showed that the value obtained from the method is within the error of the CRM. The %RSD was found to be 4.29. Accuracy of the determinations, expressed as relative error between the certified and observed values of the reference material, were $\leq 0.2\%$. The precision of these measurements, expressed as RSD for 5 independent determinations, was also satisfactory, being lower than 3% in all cases. The LOD of the Ni(II)-DMG IIP was found to be $0.0003 \pm 0.0001 \text{ mg}\cdot\text{L}^{-1}$ while the LOQ was $0.0009 \text{ mg}\cdot\text{L}^{-1}$. The recoveries of the spiked CRM samples were very good (99-100%).

Analysis of real samples

The Ni(II)-DMG IIP was then used to determine the concentration of Ni(II) in water samples (Table 6). EFs were calculated as

Wavelength (nm)	Calibration Linearity R^2	Certified concentration ($\text{mg}\cdot\text{L}^{-1}$)	Concentration found (n=3) ($\text{mg}\cdot\text{L}^{-1}$)	Relative error (%)	%RSD (n=6)	LOD ($\mu\text{g}\cdot\text{mL}^{-1}$) (n=5)	LOQ ($\mu\text{g}\cdot\text{mL}^{-1}$) (n=3)
231.60	0.9954	0.8980 (0.007)*	0.8991 (0.0013)*	+0.1225	4.29	0.0003 (0.0018)*	0.0009 (0.002)*

CRM	Certified Ni(II) conc. value ($\mu\text{g}\cdot\text{mL}^{-1}$)	Ni(II) conc. in sample ($\mu\text{g}\cdot\text{mL}^{-1}$) (n=3)	Amount of Ni(II) added ($\mu\text{g}\cdot\text{mL}^{-1}$) (n=3)	Concentration found ($\text{mg}\cdot\text{L}^{-1}$) (n=3)	% Recovery
SEP-3	0.900	0.8991	0, 5, 10	0.8991, 5.8603, 10.9052	-,99, 100

Type of water sample	^a Ni(II) conc. value in the sample ($\mu\text{g}\cdot\text{mL}^{-1}$) (digested)	^b Ni(II) conc. value obtained without digestion ($\mu\text{g}\cdot\text{mL}^{-1}$)	^c Ni(II) conc. value obtained when using Ni(II)-DMG IIP ($\mu\text{g}\cdot\text{mL}^{-1}$)	EF*	Ratio (b/a)
Sea	0.0220	0.0015	0.0265	18	0.07
Town River	0.041	0.0193	0.0546	3	0.47
Village River	0.1001	0.0112	0.1246	11	0.11
Treated sewage	0.1013	0.0181	0.1164	6	0.18
Untreated sewage	0.0339	0.0201	0.0408	2	0.59

Sample	Ni(II) ($\mu\text{g}\cdot\text{mL}^{-1}$)	Co(II) ($\mu\text{g}\cdot\text{mL}^{-1}$)	Cu(II) ($\mu\text{g}\cdot\text{mL}^{-1}$)	Zn(II) ($\mu\text{g}\cdot\text{mL}^{-1}$)	Na(I) ($\mu\text{g}\cdot\text{mL}^{-1}$)	K(I) ($\mu\text{g}\cdot\text{mL}^{-1}$)	Ca(II) ($\mu\text{g}\cdot\text{mL}^{-1}$)	Mg(II) ($\mu\text{g}\cdot\text{mL}^{-1}$)
Sea	0.0087	0.0015	0.5337	1.145	1877	3617	2035	8319
Town River	0.0417	0.0021	0.4130	1.273	833.0	128.2	477.2	512.2
Village River	0.1001	0.0035	0.2971	1.237	268.3	8.154	110.3	55.85
Treated sewage	0.1013	0.0022	0.3111	1.465	591.5	212.0	485.6	278.6
Untreated sewage	0.0330	0.0075	0.7000	1.979	677.7	245.0	487.5	278.6

shown in Eq. 3:

$$EF = \frac{c}{b} \quad (3)$$

where:

c is the Ni(II) conc. value obtained when using Ni(II)-DMG IIP ($\mu\text{g}\cdot\text{mL}^{-1}$) and
b is the Ni(II) conc. value obtained without digestion ($\mu\text{g}\cdot\text{mL}^{-1}$).

The complexity of the water sample was estimated from the ratio of concentrations obtained with and without digestion. The recoveries were very good given the complexity of the matrices, because the ratios of the Ni(II) concentration values in the sample obtained with digestion to the values of Ni(II) obtained without digestion was low. In all of the water samples the concentrations of Cu(II) and Zn(II) were higher than that of Ni(II) (as shown in Table 7), but they did not interfere with the rebinding of Ni(II) on the Ni(II)-DMG IIP. Major elements found in water, Ca(II), Mg(II), Na(I) and K(I), also did not affect the recoveries of Ni(II) using the IIP. The enrichment factor was found to range from 2 to 18. This shows that the 18-fold improvement in recoveries was achieved when using the Ni(II)-DMG IIP, a considerable improvement in terms of access to the Ni(II) by Ni(II)-DMG IIP.

Conclusions

The synthesised Ni(II)-DMG IIP was prepared for the selective determination of Ni(II) from other closely-related metal ions in complex aqueous matrices. High Ni(II) recoveries with good %RSD were obtained in the presence of closely-related cations such as Co(II), Cu(II), Zn(II), Pd(II) and Fe(II). Low LOQ and LOD, short contact time required for rebinding of the Ni(II), short time period required for preparation of the IIP, lower volume/mass of reagents used to prepare the IIP, simplicity of the synthesis of the IIP, good enrichment factors, very low interference from closely-related metal ions and small polymer mass to solution volume required for optimal uptake of Ni(II), are some of the positive characteristics that this polymer offered. The Ni(II)-DMG IIP was successfully used to trap Ni(II) ions from sea, river and sewage water, and the results were validated by analysing a CRM. Based on the results presented in this work,

the Ni(II)-DMG IIP offers a good opportunity to be used as sorbent in solid-phase extraction of aqueous samples.

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